

OFFICE OF NAVAL RESEARCH
END-OF-THE-YEAR REPORT
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-97-1-0217
PR Number 97PR03373-00

**Properties and Applications of Metal Nanoshells and their
Composite Solids**

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August 6, 1997

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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT
PART I
(start date: 1/1/97)

PR Number: 97PR03373-00

Contract/Grant Number: N00014-97-1-0217

Contract/Grant Title: Properties and Applications of Metal Nanoshells and their Composite Solids

Principal Investigator: N. J. Halas

Mailing Address: ECE Department, Rice University, 6100 S. Main, Houston, TX 77005

Phone Number: (713) 737-5611 Fax Number: (713) 524-5237

E-mail Address: halas@faraday.rice.edu http address: <http://www-ece.rice.edu/~halas/>

a. Number of papers submitted to refereed journals, but not published: 1

b. Papers published in refereed journals:

R. D. Averitt, D. Sarkar, and N. J. Halas, "Plasmon Resonance Shifts of Au Coated Au₂S Nanoshells: Insight into Multicomponent Nanoparticle Growth", Physical Review Letters **78**, 4217 (1997).

c. Number of books or chapters submitted, but not yet published: 0

d. Number of books or chapters published: 0

e. Number of printed technical reports/non-refereed papers: 0

f. Patents filed: Metal Nanoshells, # 5174-01101; March 14, 1997

g. Number of patents granted: 0

h. Invited Presentations: 3 on this topic, 6 total:

"Topics in Nanoengineering", AIChE Meeting, Southwest Texas Chapter, Beaumont, TX April 1997

"Molecular Nanoprobes and Metal Nanoshells", invited talk, Physics Department, University of Pittsburgh, Pittsburgh, PA, April 1997.

"Fullerene Nanoprobes and Metal Nanoshells", invited talk, IBM Rushlikon Laboratory, Zurich, Switzerland, May 1997.

i. Submitted Presentations: 2

“Optical Properties of Gold/Gold Sulfide Nanoshells”, R. D. Averitt, D. Sarkar, and N. J. Halas, contributed talk at the American Physical Society March Meeting, Kansas City, MO, March 1997.

“Self-assembled Metal Nanoshells”, S. J. Oldenburg, R. D. Averitt, and N. J. Halas, contributed talk at the American Physical Society March Meeting, Kansas City, MO, March 1997.

j. Honors/Awards/Prizes for contract/grant employees (list attached): 0

k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number: 1

Graduate Students: 2

Post-Doctoral Associates: 0

including the number of,

Female Graduate Students: 0

Female Post-Doctoral Associates: 0

the number of

Minority Graduate Students: 0

Minority Post-Doctoral Associates: 0

and, the number of

Asian Graduate Students: 0

Asian Post-Doctoral Associates: 0

l. Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

“Fullerene-based Thin Films and Nanometer Scale Photonic Devices”

Texas Higher Education Coordinating Board (THECB)

total amount: \$240,155

amount received this year: \$ 120,055

period of performance: 1/1/96 to 12/31/97

Relationship to ONR grant: The nanometer scale photonic devices aspect of this research supports the fabrication chemistry for metal nanoshells

“Excimers and Exciplexes in fullerene-derived solids and charge-transfer complexes”

The Robert A. Welch Foundation

total amount: \$102,000

amount received this year: \$34,000

period of performance: 6/1/95 to 5/30/98

Relationship to ONR grant: Currently this is an independent research project: however, this project will support an investigation of lifetime quenching of excitons by metal nanoshells

“Young Investigator Award”

National Science Foundation

total amount: \$ 312,500

amount received this year: \$ 62,500

period of performance: 8/15/92 to 7/31/97 (one year no-cost extension for non-federal matching funds)

Relationship to ONR grant: Provides ancillary support for metal nanoshell research in addition to other projects

+ Use the letter and an appropriate title as a heading for your list, e.g.: b. Published Papers in Refereed Journals, or, d. Books and Chapters published. Also submit the citation lists as ASCII files via email or via PC-compatible floppy disks

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

General Distribution List (abstracts only):

(PI list: Use email distribution list sent via email)

Technical Report Distribution List

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**OFFICE OF NAVAL RESEARCH
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PART II

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d. Program objective:

The major focus of this research is the “**Nanoengineering of Physical Properties of Materials**”. The goal is to learn to use molecular and nanoparticle building blocks to predictively design specific, highly controllable properties into materials that are not necessarily available in naturally occurring condensed-matter systems. The optical properties of composite nanoparticles called **metal nanoshells** are of particular interest in this context. Metal nanoshells are a new and unique type of composite nanoparticle that possesses physical properties of clear technological and defense-related importance. These properties include an extremely strong structure-dependent optical resonance that can be shifted across a remarkably broad range of the visible and the infrared regions of the spectrum. Our immediate objective is to extend our knowledge of the growth chemistry, molecular control, and optical properties of metal nanoshells and associated nanoparticle assemblies, both in dilute matrices and in nanoscale proximity to each other and to other optically active materials. This is a coordinated effort consisting of nanoparticle synthesis, molecular based assembly methods, optical characterization techniques, scanning probe microscopy, theory, and the demonstration of new functional materials and simple device structures.

e. Significant results during last year -

We have performed a detailed investigation of the optical properties of gold-terminated gold sulfide nanocrystals, a naturally occurring metal nanoshell system. We have shown that the plasmon-related

absorption resonance is purely classical in origin and is determined solely by the relative thickness of the Au shell and the Au₂S core diameter. Our understanding of the optical properties of these nanoparticles was then used to elucidate the nanoparticle growth kinetics.

In order to obtain control over the optical resonances of these types of nanoparticles, we have developed an approach to the construction of metal nanoshell particles which combines the techniques of molecular self-assembly with the reduction chemistry of metal colloid synthesis. We have successfully produced silica core, gold shell metal nanoshell particles in this manner. The symmetry and size uniformity of the core and shell of these nanoparticles is precise enough to permit extremely close agreement between classical electromagnetic scattering theory (Mie scattering) and the UV-visible absorption of these nanoparticles, using the nanoparticle core and shell thicknesses determined from TEM measurements. These nanoparticles can serve as constituents in a new class of materials that are capable of uniquely controlling radiation in the visible and infrared spectral regions.

f. Summary of plans for next years work:

Research in the next year will focus both on synthesis aspects and physical measurements of metal nanoshells and related composite nanoparticles. By varying the core-shell thickness ratio during metal nanoshell fabrication, we plan to extend the optical resonances of metal nanoshells further into the infrared, toward the 3-5 micron range. We also plan to synthesize and study small, well-controlled assemblies of metal nanoparticles (2-100) bonded to dielectric nanoparticle surfaces, obtained by varying the growth procedure for metal nanoshells. We plan to investigate the dynamical optical response of metal nanoshells via femtosecond optical measurements. We also plan to develop additional spectroscopic probes of composite nanoparticles, to characterize the binding strength and number of molecular linkages between constituent nanoparticles. These probes will focus on (a) the terahertz and subterahertz resonances of nanoparticle vibrational spectroscopy, and (b) the large modifications in the vibrational excitations of α,ω functionalized linker molecules that occur when these molecules are "tethered" between two nanoparticles. In addition, we will begin to investigate the use of metal nanoshells in modifying the photophysics of conducting polymer matrices. We will also pursue technology transfer of metal nanoshell mixtures.

g. List of names of graduate students and post-doctoral(s) currently working on the project:

1. Steven J. Oldenburg: supported by ONR
2. Sarah L. Westcott: supported by an NSERC (Canada) Scholarship
3. Richard D. Averitt: supported by NSF
4. Young Seok-Shon: supported by ONR
5. Lon A. Porter (undergraduate)

Properties and Applications of Metal Nanoshells

and their Composite Solids

Halas/Lee, Rice/UH

Technology Issues:

to nanoengineer new materials for imaging, thermal management, and obscurant-related applications

Objectives:

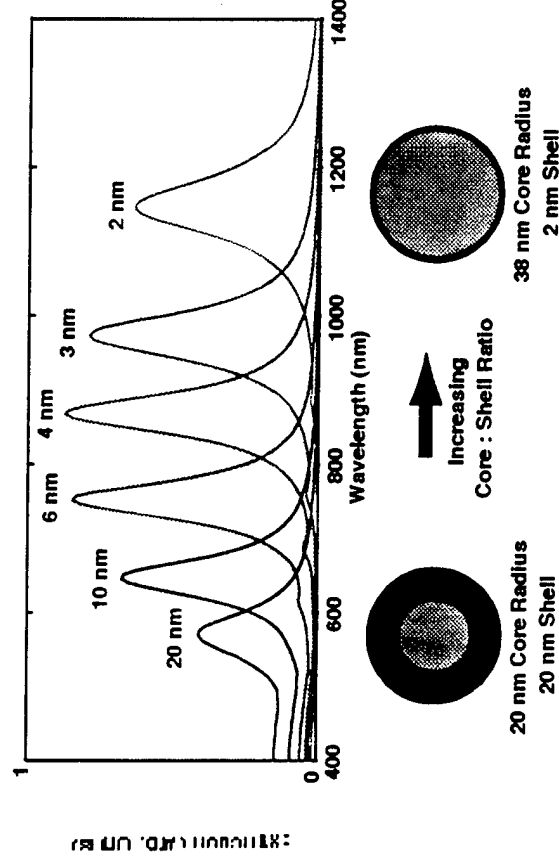
the development and demonstration of new functional materials and simple device structures based on *metal nanoshells*

Accomplishments:

- a comprehensive understanding of the optical properties of naturally occurring metal nanoshells
- a general fabrication method for metal nanoshells

Approach:

a coordinated effort consisting of nanoparticle synthesis, molecular based assembly methods, optical characterization techniques, scanning probe microscopy, theory, and the demonstration of new materials and devices

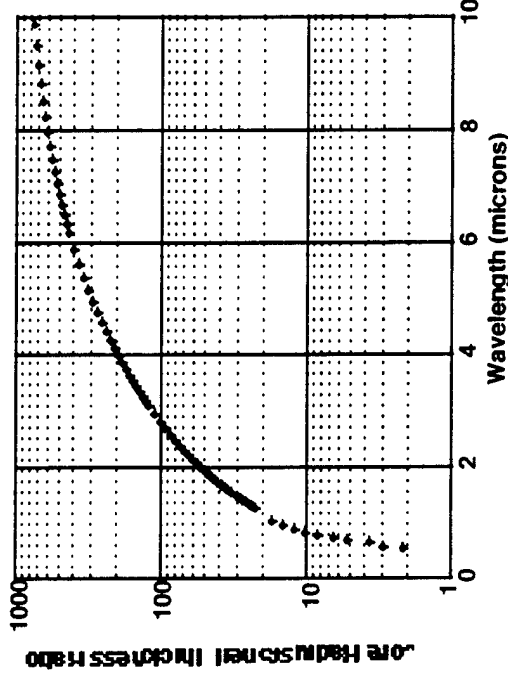
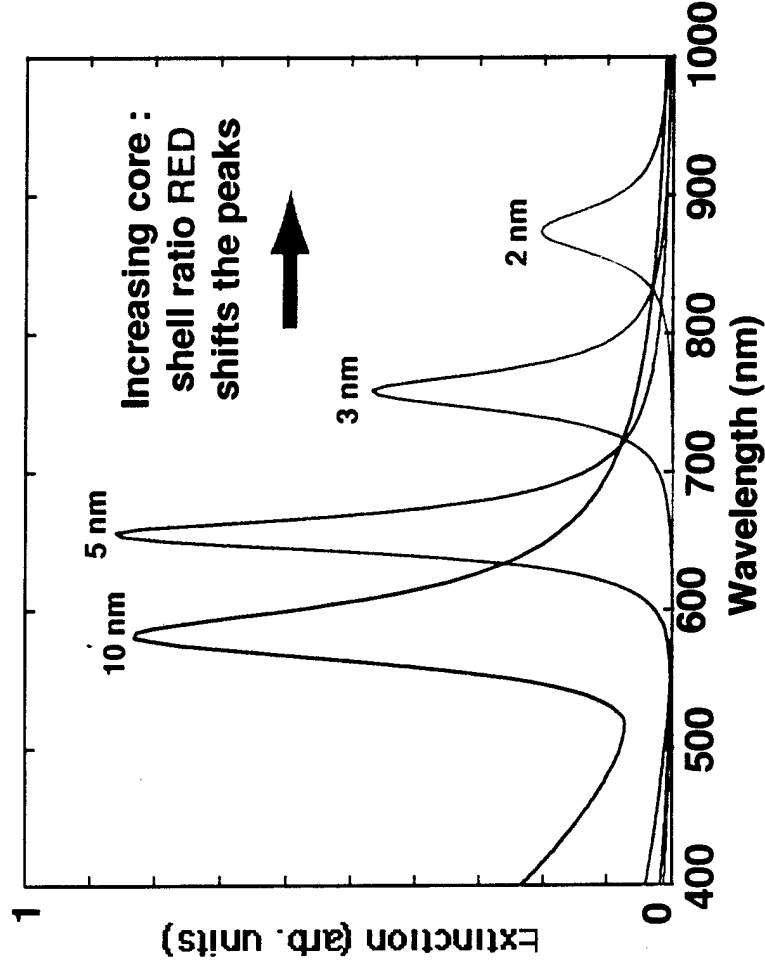


Impact:

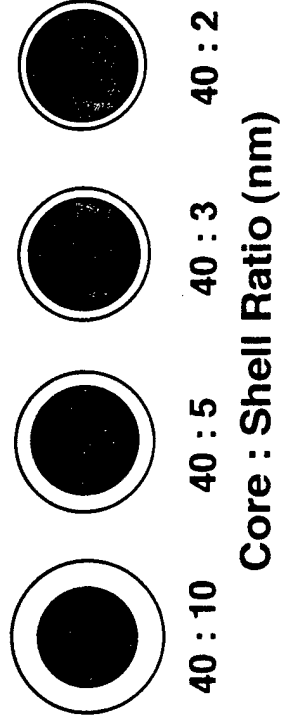
a new class of optical materials whose optical resonances can be "designed in" over a large region of the electromagnetic spectrum and placed at the optimal desired wavelength for specific visible and infrared applications

Optical Properties of Metal Nanoshells

Halas/Lee, Rice/UH



Control of core-shell ratio can shift the resonance of metal nanoshells across the visible and the infrared regions of the spectrum.

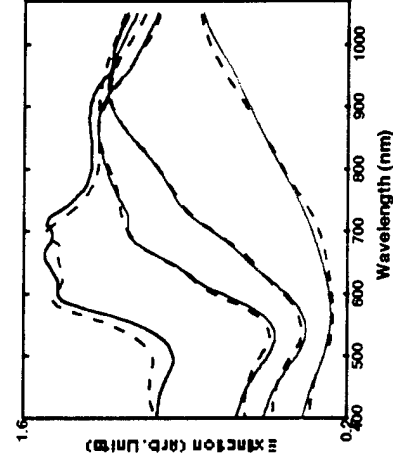
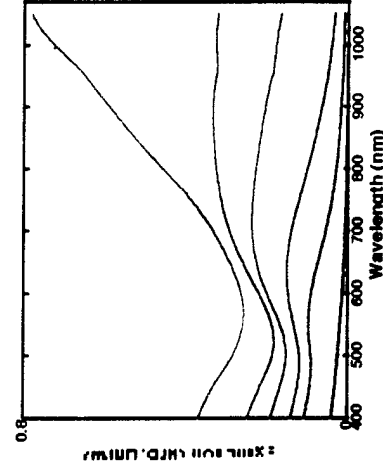


Metal Nanoshell Fabrication

Halas/Lee, Rice/UH



This sequence of TEM images follows the metallization of a 100 nm silica nanoparticle initially “decorated” with gold seed colloid of 1-2 nm diameter..



Both the coalescence (left figure) and the continued growth (right figure) of the metal nanoshell yields a distinct, structurally-dependent optical signature that agrees very well with classical electromagnetic scattering theory (Mie scattering).

Part III

Viewgraph 1:

The major theme of this proposal is the development of materials with new functionalities that can be *designed in* at the nanometer scale level. This quite broad scope has, in reality, a very specific and practical focus: to develop, investigate, and technologically exploit the properties of a new type of composite nanoparticle that we call *metal nanoshells*. These nanoparticles consist of a dielectric or semiconductor core and a metallic shell of nanometer scale thickness. These nanoparticles have the unique quality that their plasmon derived optical resonance is a function of their core diameter and their shell thickness. In other words, by varying the thickness ratio between their core and shell one can place the optical resonance of the particle at any wavelength you choose over a very broad wavelength range. This figure illustrates 40 nm radius composite nanoparticles constructed of a silica core and a gold shell. For the same total particle radius, varying the core/shell thickness ratio as shown allows one to shift the optical resonance of these nanoparticles over a 500 nm wavelength range. If the dielectric core and the metal shell were reversed, the total wavelength shift would be only 20 nm. This type of composite nanoparticle opens up new and very flexible possibilities for *nanoengineering optical resonances* of materials. This project serves as a connection between nanoparticle photophysics, the colloidal and molecular growth chemistry inherent in composite nanoparticle synthesis, appropriate laser-based and nanoprobe-based characterization techniques, and the construction of new prototype materials and devices in which metal nanoshells and related composite nanoparticles play an important functional role.

Viewgraph 2:

An initial accomplishment of this program was achieving an accurate and detailed understanding of this structure-dependent optical resonance shift, as well as the linewidth broadening mechanisms of metal nanoshell resonances. The resonance shifts are determined exclusively by classical electromagnetic scattering theory, or Mie scattering, and the predominant line broadening mechanism is due to confinement of the electrons in the thin shell region. Since this is classical Mie scattering, the amplitude of the extinction (absorption plus scattering) is determined by the ratio of the total particle diameter to the wavelength of incident light. This is shown in the leftmost figure: while the core-shell ratio shifts the nanoparticle resonance into the infrared, the ratio of the total particle size to the wavelength gets smaller, resulting in a particle which is predominantly an absorber (dipole scatterer). Thus we can also design whether the particle will be an absorber or a scatterer at its resonance wavelength. Here we also show a theoretical range for shifting metal nanoshell optical resonances, calculated specifically for silica-gold nanoshells. Although the resonance properties become weaker at longer wavelengths, for core-shell ratios of 20 to 500 one should be able to tailor resonances of nanoparticles throughout the near-IR and the mid-IR range of the spectrum.

Viewgraph 3:

Another initial accomplishment of this research program is the development of a fabrication method for silica-gold metal nanoshells. Prior to this procedure, our work focussed exclusively on metal nanoshells that occurred naturally in the nanoparticle growth process. This method enables us to independently control the core size and composition, and to control the shell composition and growth. A series of TEM images taken at various stages during the nanoshell metallization stage is shown here. This stage starts with the adsorption of very small (1-2 nm) gold nanoparticles onto the silica nanoparticle surface. This structure itself is a very important initial starting point for other types of composite nanoparticles with optical resonances in yet other regions of the electromagnetic spectrum. Once this nanoparticle has been prepared in this manner, it is subjected to standard gold reduction chemistry, which causes the coalescence of the gold nanoparticles and the growth of a continuous gold shell. The optical signature of the coalescence corresponds very well to previous experimental observations of light scattering from gold platelets; once the nanoshell has been formed, its optical properties correlate very closely with Mie scattering for the same size core and shell nanoparticles.

Properties and Applications of Metal Nanoshells

Hales/Lee, Rice/UH

and their Composite Solids



by Lee

to engineer new materials for increasing thermal management, and obscureant-related **NEW PARADIGM**

Objectives: This sequence of TEM shifts the peaks the metalization of 100 nm silica seed colloids of 2 nm diameter.

metal nanoshells

Accomplishments:

- a comprehensive understanding of the optical properties of naturally occurring metal nanoshells
- a general fabrication method for metal nanoshells

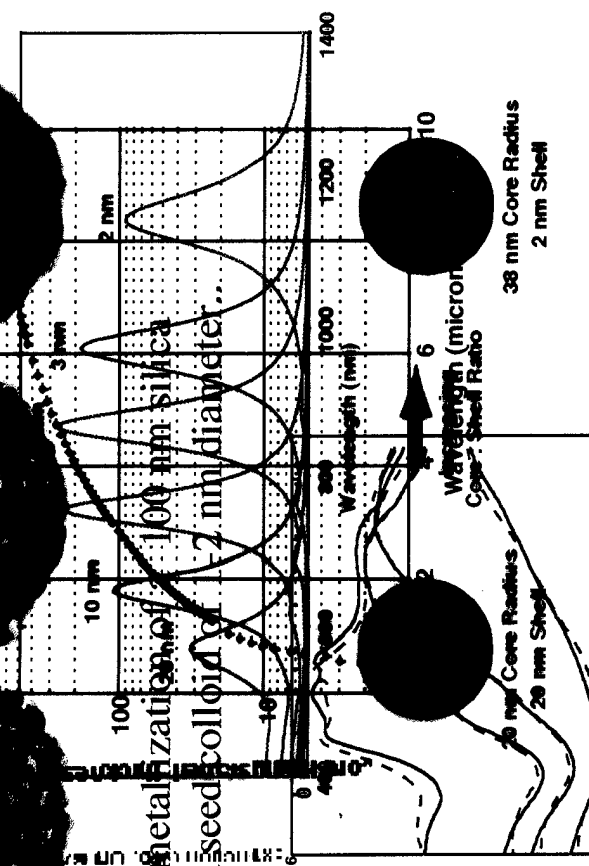
App 100 ch: 500 **Wavelength (nm)** 600 700 800 900 1000 1100 1200 1300 1400

a coordinated effort consisting of nanoparticle

synthesis and characterization of nanoshells. The continued growth of the nanoshells is dependent on the optical properties of the electron materials, specifically in the infrared region of the spectrum. The optical properties of the nanoshells are placed in the context of the desired wavelength for specific visible and infrared applications

40 : 10 40 : 5 40 : 3 40 : 2

Core : Shell Ratio (nm)



Impact: Control of core-shell ratio can shift a new class of optical materials whose optical resonances can be designed in the infrared region of the spectrum and the optical properties of the nanoshells are placed in the context of the desired wavelength for specific visible and infrared applications